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Electronic Effects in Organometallic Complexes.

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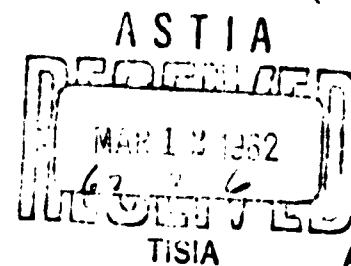
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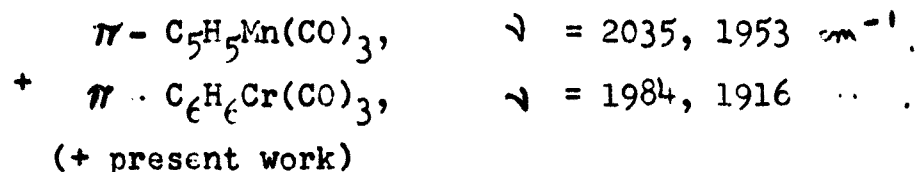


Electronic Effects in Organometallic Complexes.

The nature of the bonding in many organometallic systems can be understood in terms of molecular theory¹ and arises essentially from the interaction of the s,p and d orbitals of the central metal atom with the π orbitals of the conjugated system.

The application of such theory² to complexes of the type $C_nH_nMY_m$ where $n = 4---8$, M is a transition metal and Y a ligand leads to the prediction of increasing charge transfer from the ring system to the central metal atom as n increases from 4 to 6 within isoelectronic complexes. This result follows from the nature of the interactions between C_nH_n with a ground state a^2 , e^x , e_2^y ($x = 2---4$, $y = 0---2$) and the metal orbitals under the local symmetry D_n ($n = 4...$); the interactions will be of the type (a , $4s/4p$), (e , $3d/4p$), and (e_2 , $3d$). The first of these must lead to charge transfer to the central metal atom since the totally-symmetric orbital is always filled but the extent of charge transfer in the other two will depend upon x and y. Thus for a cyclopentadienyl complex, $n = 5$, $x = 3$, $y = 0$, there will be some charge transfer to the metal but less than for a benzene complex, $n = 6$, $x = 4$, $y = 0$, since the e_1 interaction in the latter is between a filled π orbital and empty metal $3d/4p$ hybrids. In both cases there will be back-donation from the metal to the empty e_2 orbitals but the dominant factor will be the difference in the e_1 class. For complexes in which the ligand Y is a carbonyl

the extent of charge transfer is reflected in the carbonyl stretching frequencies; the greater the negative charge on the metal atom M, the greater the transfer to the vacant orbitals of the carbonyl group and hence the lower the C-O stretching frequency. This is illustrated by the sequence³:-



In this paper we wish to discuss the transmission of electronic effects due to the substituent X in complexes of the type $\pi - \text{XC}_6\text{H}_5 - \text{Cr}(\text{CO})_3$. The nature of this effect will be first considered in terms of molecular orbital theory analogous to that of the introductory discussion. The theoretical results are then compared with experimental evidence both from the carbonyl stretching frequencies and from solvent effects upon the same.

Molecular Orbital Theory

As a model for the complex $\pi - \text{X} - \text{C}_6\text{H}_5\text{Cr}(\text{CO})_3$, we assume the structure shown in Figure 1 in which the plane of the aromatic ring is parallel to the xy-plane containing the chromium atom; this structure is known to be correct for the unsubstituted compound.⁴

Fig. I

The three carbonyl groups possess C_{3v} local symmetry whilst the aromatic component possesses only C_{2v} local symmetry. The σ -orbitals of the $(CO)_3$ group fall therefore into the representation $A_1 + E$ whilst the π orbitals fall into $A_1 + 2B_2$. The symmetry classification of the interaction of these orbitals with the central metal s,p and d orbitals in the above complex is given in Table I

Table I

Symmetries of Constituent Orbitals in Complex $-XC_6H_5Cr(CO)_3$

XC_6H_5 Orbitals	Metal Orbitals	Ligand Orbitals
$1a_1$	$(4s)$	a_1
$2a_1$	$(4p_z)$	
$3a_1$	$(3d_{z^2})$	
$4a_1$	$(3d_{xz})$	e_x
$5a_1$	$(4p_x)$	
	$3d_{xy}$	e_y
	$3d_{x^2-y^2}$	
$1b_2$	$3d_{yz}$	
$2b_2$	$4p_y$	

A quantitative estimate of the above interactions is given first by the various group overlap integrals and, secondly

by the differences in the Coulomb terms of the respective orbitals. These were evaluated for the above system for two extreme cases in which (a) X is assumed to be highly electronegative, that is an electron-attracting substituent (+E on Dewar Notation) and (b) X is assumed to be highly electropositive that is an electron-donating substituent (-E). These cases were obtained by evaluating the molecular orbitals for the molecule C_6H_5X in which the Coulomb term of the heteroatom X and its resonance integral with an adjacent C ($2p_\pi$) orbital are given by:-

$$\begin{aligned} H_{xx} &= H_{cc} + m\beta_{cc} \\ H_{cx} &= n\beta_{cc} \end{aligned}$$

The parameters m and n were assigned the values $m = +2.0$ and $n = 1.00, 1.80$ which cover the two extreme type of substituent. The coefficients of the isolated molecular orbitals were then obtained by standard procedure. The group overlap integrals between these π orbitals and the various metal orbitals were calculated for the above model in which the Cr - C₁ ($\phi = 1$ ---6) distance was taken as 2.25\AA ,⁴ and the Cr - X distance as 3.31\AA , this latter distance is that calculated for the chlorobenzene complex but since the overlap integrals are relatively insensitive to small differences in this distance

the results are generally applicable. The chromium atom was assigned the configuration $3d^4 4s^2$ and the screening constants of the Slater $3d, 4s$ and $4p$ orbitals calculated accordingly. The formulae used for calculating the group overlap integrals were identical with those derived in earlier papers⁵ but as an illustration we give below the formula for the overlap integral between a totally - symmetric π -orbital and the $4p_z$ orbital of chromium

$$S(\psi, 4p_z) = \sum_{i=1}^7 c_i [S_i(2p_\sigma 4p_\sigma) \cos^2 \theta_i - S_i(2p_\pi 4p_\pi) \sin^2 \theta_i]$$

where c_i is the coefficient of i th carbon atom in the given molecular orbital and θ_i the angle between the Z axis and the $M - C_i$ vector. The constituent overlap integrals, viz $S(2p_\sigma 3d_\sigma)$, $S(2p_\pi 3d_\pi)$, $S(2p_\sigma 4s)$, $S(2p_\sigma 4p_\sigma) + S(2p_\pi 4p_\pi)$ were obtained by interpolation from the tables of Jaffé, Cotton et al and Brown⁶ respectively. The results are given in Table 2. The group overlap integrals involving the $4p_z$ and $3d_{z^2}$ orbitals were found to be small for the complete range of the parameters m and n . The anti-symmetric orbitals are independent of the substituent and so do not contribute to any difference in electronic effects in the substituted systems. We also give

in Table 2 in parentheses the differences in the Coulomb terms of the π orbitals and of the chromium orbitals. The latter were obtained from spectroscopic data⁷ and the former by identifying the first ionization potential of benzene with the Coulomb term of the highest filled orbital, $H(e_1e_1)$. The various terms for the two cases of substituents were then obtained from the respective roots taking the resonance integral β_{cc} as 2.5 e.v.⁵ This procedure does not, of course, give reliable absolute values for these terms but it should provide a reasonable scale of values.

Table 2

Group Overlap Integrals and Coulomb Term Differences

m	n	ψ	$S(\psi, 4s)$	$S(\psi, 4p_x)$	$S(\psi, 3d_{xz})$	$S(\psi, 3d_{xy})$	$S(\psi, 3d_{x^2-y^2})$
+2.0	1.0	$1a_1$	0.151 (5.8)	0.146 (8.2)	0.092 (6.5)	0.044 (6.5)	-
-2.0		$1a_1$	0.211 (4.3)	0.026 (6.9)	0.019 (5.0)	-	-
+2.0	1.0	$2a_1$	0.150 (4.4)	0.119 (6.2)	0.032 (4.5)	-	-
-2.0		$2a_1$	0.008 (2.0)	0.258 (4.5)	0.268 (2.7)	-	0.090 (2.7)

/over

Table 2 (contd).

m	n	ψ	$S(\psi, 4s)$	$S(\psi, 4p_x)$	$S(\psi, 3d_{xz})$	$S(\psi, 3d_{xy})$	$S(\psi, 3d_{x^2-y^2})$
+2.0	1.0	$3a_1$	-	0.183 (3.6)	0.238 (1.8)	-	0.094
-2.0		$3a_1$	-	0.007	0.027 (-2.0)	0.161 (-2.0)	-
+2.0	1.0	$4a_1$	-	-	-	0.157 (-2.8)	-
		$4a_1$	-	-	-	0.040 (-4.5)	0.122 (-4.5)
+2.0	1.0	$5a_1$	-	-	-	-	0.132 (-5.1)
		$5a_1$	-	-	-	-	0.059 (-6.5)
+2.0	1.80	$1a_1$	0.136 (7.4)	0.164 (9.9)	0.113 (8.1)	0.054	-
-2.0		$1a_1$	0.207 (4.7)	0.076 (7.2)	0.063 (5.4)		
+2.0	1.80	$2a_1$	0.164 (3.6)	0.124 (6.1)	0.112 (4.3)	-	-
-2.0		$2a_1$	0.046 (2.50)	0.248 (5.0)	0.251 (3.26)	-	0.078
+2.0	1.80	$3a_1$	-	0.163 (2.96)	0.218 (1.20)	0.060 (1.20)	0.098 (1.20)
-2.0		$3a_1$		0.039 (0.52)	0.080 (-1.23)	0.155 (-1.23)	0.055 (-1.23)
+2.0	1.80	$4a_1$	-	-	-	0.142 (-3.30)	0.051 (-3.30)
-2.0		$4a_1$	-	-	-	0.057 (-4.41)	0.127 (-4.41)
+2.0	1.80	$5a_1$	-	-	-	-	0.119 (-5.50)
-2.0		$5a_1$	-	-	-	-	-

/over

Table 2 (contd)

Benzene	ψ	$S(\psi, 4s)$	$S(\psi, 4p_x)$	$S(\psi, 3d_{yz})$	$S(\psi, 3d_{xy, x^2-y^2})$
Substituent X absent	a_1	0.207 (4.2)	-	-	-
	e_1	-	0.244 (6.7)	0.271 (2.5)	-
	e_2	-	-	-	0.165 (-2.5)

Consider first the interactions between the filled totally symmetric π orbitals ($1a_1$ --- $3a_1$) of C_6H_5X and the empty $4s, 4p_x$ and $3d_{xz}$ orbitals of the chromium atom for the two extreme cases $m = +2.0$ and -2.0 . In the case of the $1a_1$ orbital the interactions with the $4p_x$ orbital will be small in view of the large difference in Coulomb terms. The integral $S(1a_1, 4s)$ is greater for $m = -2.0$ than $m = +2.0$ whilst the ΔH value is smaller. For the interaction ($1a_1, 3d_{xz}$) the integral is smaller but so is the ΔH value. The predominant interaction is greater then for $m = -2.0$ than $m = +2.0$, hence greater charge transfer will occur from the filled π orbitals to the empty metal orbitals. Similar arguments apply to the interactions ($2a_1, 4p_x$) and $2a_1, 3d_{xz}$). However, the reverse conclusion is true in the case of the $3a_1$ orbital, since here the interactions are greater and the ΔH values smaller for $m = +2.0$ than for $m = -2.0$. Now consider

the interaction of the empty $4a_1$ and $5a_1$ orbitals with the filled $3d_{xy}$ and $3d_{x^2-y^2}$ chromium orbitals. For both orbitals the overlap integrals are greater and the DH values smaller for $m = +2.0$ than for $m = -2.0$. In other words there will be greater back-donation from the chromium atom to the empty π^* -orbitals of the C_6H_5 system in the case of $m = +2.0$ than in $m = -2.0$. We conclude from these arguments then that for both electron donating and electron accepting substituents there will be charge transfer to the chromium atom but that it will be greater for the electron donating substituent ($m = -2.0$). It is apparent from table 2 that the above arguments are in fact equally if not more valid for the case $n = 1.80$ than for $n = 1.00$.

The above conclusions based on the molecular orbital theory of these complexes supports a more naive chemical approach which considers the complex to be equivalent to a conjugated system. The transmission of electronic effects through such systems containing both π orbitals and central metal orbitals is then seen to be similar to those observed in simple conjugated molecules.

Comparison with Experiment

In a complex containing carbonyl groups as simple ligands any negative charge accumulated on the central metal atom will be dispersed in accordance with the Pauling electroneutrality principle by back-donation to the carbonyl groups. This donation

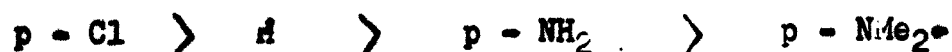
will lead to an increase in the metal - carbon bond order and to a lowering of the carbon - oxygen bond order and hence to a decrease in the carbonyl stretching frequencies. Accordingly, the carbonyl frequencies of a number of substituted complexes, π -X-C₆H₅Cr(CO)₃, were measured in solution and compared with those of the unsubstituted complex and of chromium hexacarbonyl itself. The measurements were made on solutions in cyclohexane, chloroform, carbon tetrachloride and dichloroethane. The bands were in general quite sharp but a splitting of the lower frequency was often observed for the substituted compounds; this is presumably due to the lifting of the degeneracy in the trigonal (CO)₃ group in the presence of a substituent (see Figure 1). Where comparison is available, the results agree well with those of Fischer³; the maximum difference is 2 cm⁻¹ and this is probably the limit of accuracy of the measurements. The results are given in Table 3.

Table 3

Carbonyl Frequencies of Cr(CO)₆ and arene Cr(CO)₃ complexes
Frequencies to ± 2 cm⁻¹

Solvent	Cr(CO) ₆	ClC ₆ H ₅ -Cr(CO) ₃	(C ₆ H ₆)Cr(CO) ₃	NH ₂ C ₆ H ₅ -Cr(CO) ₃	NMe ₂ -Cr(CO) ₃
C ₆ H ₁₂	1987	1992 1930 1926	1984 1916	1974 1902	1969 1895 1889
CCl ₄	1988	1990 1925 1923	1983 1910	1971 1895	1968 1887
CHCl ₃	1984	1985 1914	1977 1900	1965 1884	1959 1876
C ₂ H ₄ Cl ₂	1982	1980 1905	1972 1892	1959 1874	1946 1866

It is immediately obvious that, independent of the solvent and of the type of band, the C=O frequencies, ν (C = O), lie in the sequence:-



which is in agreement with the above theoretical predictions; that is, the greater the electron-donating power of the substituent, the greater the charge transfer to the chromium atom and hence the lower the carbonyl frequency. Attention has already been drawn by Fischer³ to the correlation between the carbonyl stretching frequency and the dipole moment of a complex⁸; this correlation provides further support for the theory.

Solvent Effects

In a recent paper, Nyholm et al⁹ drew attention to the effect of solvents upon the carbonyl stretching frequencies of both simple and substituted metal carbonyls. It was found, for example, that in complexes of the type $\text{MD}(\text{CO})_4$, where D is O-phenylenebisdimethylarsine, the carbonyl frequency is far more sensitive to the polarity of the solvent than in the simple carbonyls. The effect was considered as being most probably due to a dipole-dipole type of interaction so that increasing back-donation to a carbonyl group will increase the solvent effect. We have used the same criterion to corroborate the charge effects in the complexes considered above as shown in Table 3.

The frequency shifts of the different carbonyl bands as

between cyclohexane and the other solvents is given in Figure 2 for the above series of substituents. Although the differences between these shifts are sometimes within experimental error the same trend is observed for all frequencies and fully supports the conclusions based upon the absolute positions of the frequencies. It is interesting that the solvent effect is greater for the degenerate mode than the totally symmetric.

It follows then that the solvent effect is a useful measure of the charge distribution in these complexes and provides further support for the theoretical predictions. Direct comparison with the metal carbonyl is not strictly valid but it is noteworthy that for all the complexes the solvent effect is greater than that for the simple carbonyl.

The above results also lend support to a theory of solvent effects proposed by Pullin¹⁰. According to this theory the frequencies ν_r and ν_g of two vibrational modes of a molecule in a series of non-polar solvents should be linearly related since all contributions to them are assumed proportional to $\frac{1}{\epsilon}$ solvent function. This latter is closely related to the term $\frac{2(\epsilon-1)}{2\epsilon+1} \frac{1}{a^3}$

derived for a model of solute-solvent interactions in which the solute molecule is considered as a point dipole at the centre of a spherical cavity of radius a in a dielectric constant ϵ . The plot of $\nu(\lambda_1)$ against $\nu(E)$ in Figure 3 for the unsubstituted complex supports the above argument; the effect of increasing

polarity of solvent does not apparently lead to much error in this case. Similar linearity is observed for the substituted complexes.

Experimental

The arene chromium tricarbonyl complexes were prepared according to the method of Nicholls and Whiting.¹¹ It was found that careful deoxygenation of solvents and the use of reaction temperatures below 130°C greatly reduced the decomposition of the complex during reaction. The compounds were purified either by sublimation or recrystallization from dry ether. Melting points agreed with those of the above authors ~~same~~ for the dimethylaniline complex (138-139° compared to 145-146°). Cyclohexane was distilled through^a a 12' column under nitrogen and the remaining solvents were purified by standard methods.¹² The infra-red spectra were measured on a Perkin-Elmer 21 instrument using lithium fluoride optics; dilute solutions (10^{-3} - 10^{-4} M) were employed.

N - H stretching frequencies

The N - H stretching frequencies of solutions of aniline, aniline chromium tricarbonyl and p-toluidine chromium tricarbonyl in carbon tetrachloride solution were measured. A concentration of 0.002 M was employed so as to preclude any difficulties arising from intermolecular H-bonding. Lithium fluoride optics were used

and calibration was made by means of a polystyrene film and water vapour covering the region from 2.5 μ to 3.6 μ . The results are compared with those for the unsubstituted compounds obtained by Califano and Moccia¹³ in Table 4

Table 4

N - H frequencies of Amine Complexes in cm⁻¹

Compound	Present Work	Califano and Moccia
Aniline	3479	3478
	3396	3395
Aniline Cr(CO) ₃	3478	-
	3393	-
p-Toluidine	-	3469
	-	3388
p-Toluidine Cr(CO) ₃	3472	-
	3390	-

It follows from these results that the formation of the complex $\text{XC}_6\text{H}_5\text{---Cr(CO)}_3$ has little effect upon the N - H stretching frequencies of the substituent X. This result is in

contrast to the behaviour of p-substituted anilines¹⁴ in which it is found that both N - H frequencies are a direct function of the electronic character of the p-substituent as evidenced by its Hammett ρ value. Obviously the formation of a π complex of the above type means that a direct correlation between the electron density at the Nitrogen atom and the N - H frequency no longer holds. The reason for this fact is not clear; it may arise from a slight change of hybridization at the N atom on complexing. That a reduction in density does occur seems well proven from the preceding discussion so that the above results are anomalous.

pKa values of Aniline Complexes

Attempts were made to determine the pKa values of the aniline and dimethylaniline chromium tricarbonyl complexes in 50% aqueous ethanol as suitable solvent. Initial determinations employing the potentiometric titration were abandoned in view of intermolecular hydrogen bonding which occurred at the concentrations employed in this method. The spectrophotometric method was found more suitable except that for the above complexes rapid decomposition occurred in acid solution. If it assumed, however, that the initial reaction is that of protonation and the subsequent reaction that of decomposition then by constructing tangents to the curve of optical density (at 3150 μ and 3175 μ respectively) against time,

it is possible to obtain a value of the indicator ratio:-

$$\frac{\text{Conc. of protonated base}}{\text{free base}}$$

The pKa values so obtained are given below in Table 5.

Table 5
pKa values in 50% Aqueous Ethanol

Compound	Mean pKa
Aniline	4.10
Aniline-Cr(CO) ₃	1.15
Dimethylaniline	4.14
Dimethylaniline-Cr(CO) ₃	1.77

Some caution is required in interpreting the above data since the above decomposition reaction is only just being studied. However, if the above assumptions are correct then the pKa values so obtained are in both cases considerably lower than those for the free amines. In other words ease of addition of a proton to the nitrogen atom is reduced, that is, the electron density at the nitrogen atom is considerably lower in the complex than in the free amine. This is again in accord with the theoretical predictions.

Acknowledgments

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Figure 1: The Complex $\bar{N}-X-C_6H_5-Cr(CO)_3$.

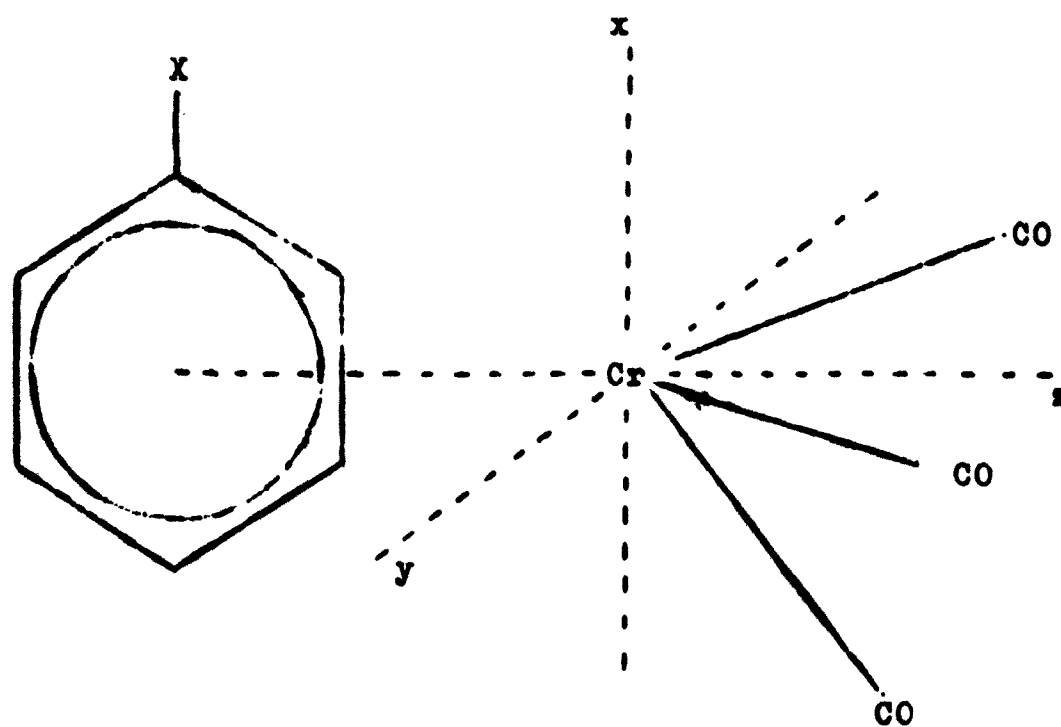


Figure 2: Solvent Effects on C=O Frequencies.

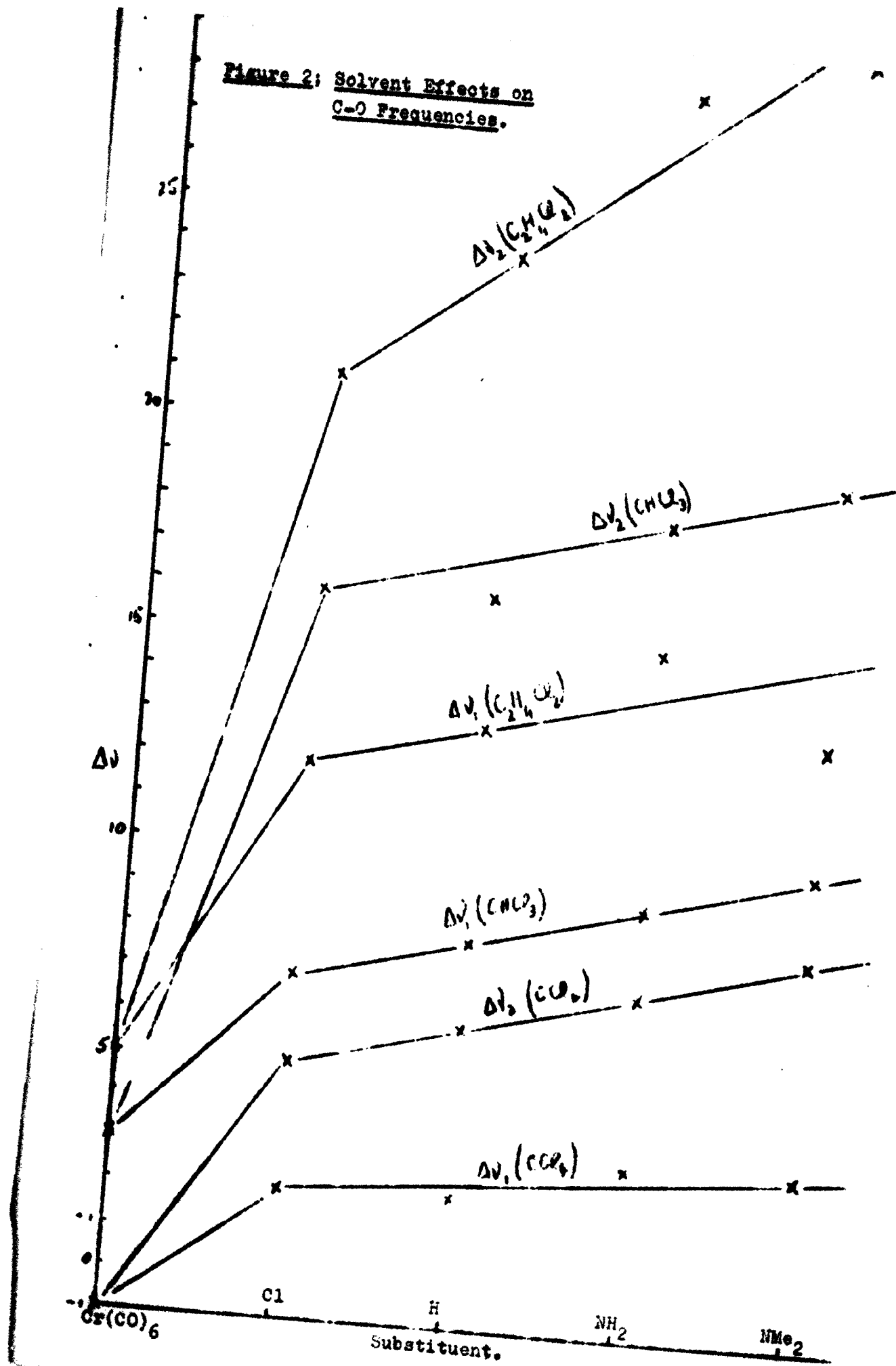
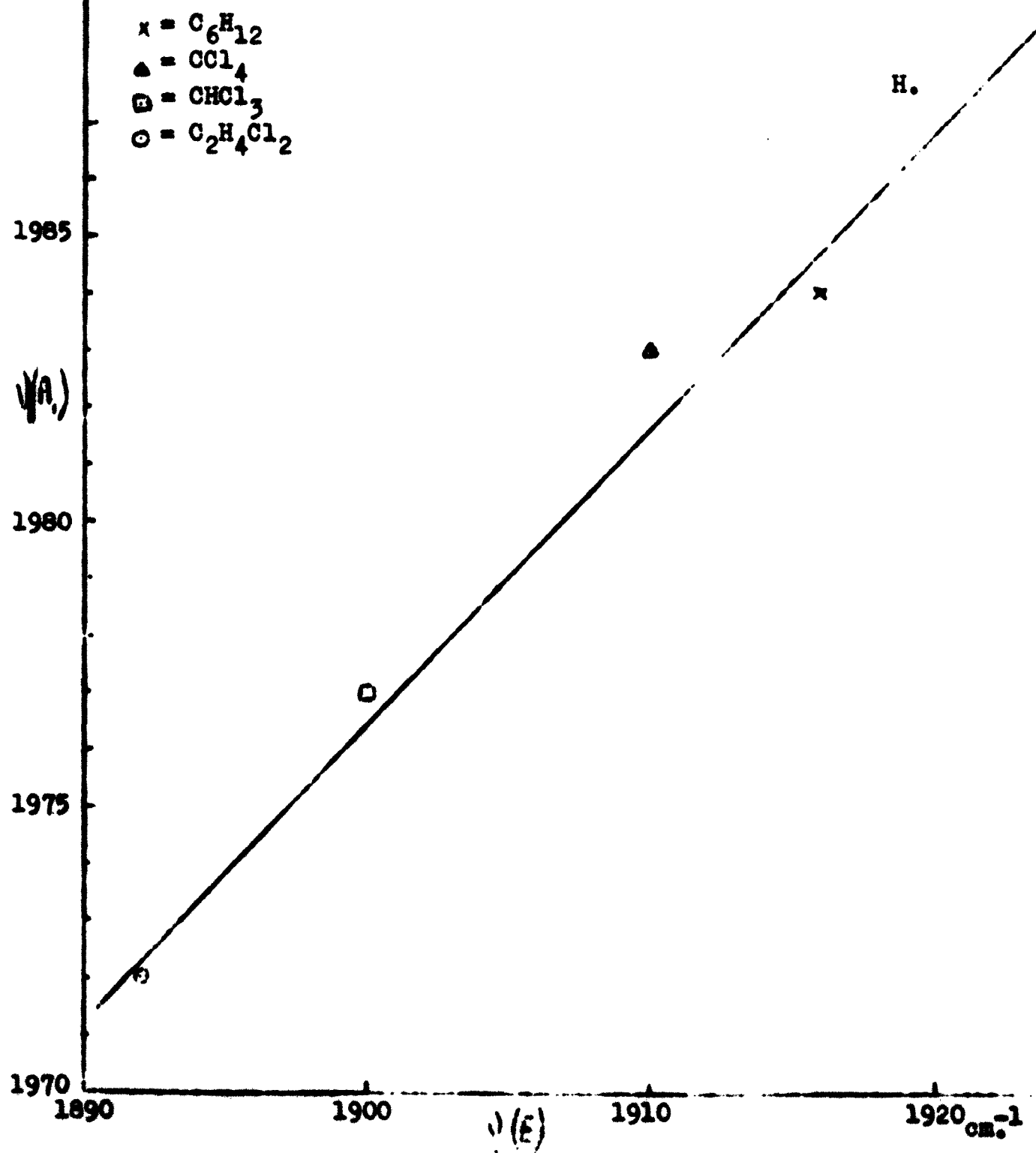


Figure 3: Relation of Carbonyl Frequencies.



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